

# Photoelectron Spectra, Penning Ionization Electron Spectra, and Character of Canonical Molecular Orbitals

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**ABSTRACT:** When canonical molecular orbitals are expanded in terms of a set of localized molecular orbital building blocks, called bond orbitals, the character of the canonical molecular orbitals can be characterized according to the component bond orbitals resembling the core, lone pair, and localized bond building blocks in an intuitive Lewis structure. Weinhold's natural bond orbital method can produce a unique Lewis structure with total occupancy of its occupied bond orbitals exceeding 99.9% of the total electron density for simple molecules. Two useful indices, Lewis bond order and weight of lone pair orbitals, can be defined according to the weights of the bonding and lone pair components of this unique Lewis structure. Calculation results for molecules  $N_2$ , CO, CS, NO, HCN,  $C_2H_2$ ,  $H_2O$ , and  $H_2S$  show that the former index can account for the vibrational structures of photoelectron spectroscopy, whereas the latter index can account for the band intensity enhancement of Penning ionization electron spectroscopy. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 882–892, 1998

**Keywords:** photoelectron spectroscopy; bond order; through bond interaction; Lewis structures; vibrational structures; natural bond orbitals

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## Introduction

**D**elocalization of  $\pi$ -orbitals in conjugated systems is familiar to chemists. Recently,  $\sigma$ -orbital delocalization has also been emphasized. Jorgensen and Salem<sup>1</sup> have shown that the canonical molecular orbital (CMO) plots of the Hartree–Fock (HF) wave function consist of only a few localized molecular orbital (LMO) building blocks. The interaction among these LMOs gives rise to orbital delocalization for both  $\sigma$  and  $\pi$  types.<sup>1</sup>

The intuitive valence bond (VB) structures (or Lewis structures) consisting of core, lone pair, and bonding-type LMOs, called bond orbitals (BO), are suited to account for chemical formulas and chemical structures. The CMOs having their orbital energies as the eigenvalues of the Fock operator are suited to account for the interaction of radiation with the molecules.

At the lowest level of the MO and VB theories, prediction of the two theories might not show agreement. In this study, we show that, when a proper BO set is chosen as a building block to form the CMO, the bond order predicted by simple MO theory will be in complete agreement with that of simple VB theory. The total bond order (the number of covalent bonds) of a simple molecule can easily be counted according to the number of bond lines in the Lewis structure. The VB theory simply relates each bond line in the Lewis structure to a doubly occupied BO  $\sigma_{AB}^2$  (or  $\pi_{AB}^2$ ) in a BO configuration. Therefore, one can easily count the total bond order of a BO configuration in the following manner: each doubly occupied  $\sigma_{AB}^2$  (or  $\pi_{AB}^2$ ) should contribute a bond order value of 1 and all other BOs of cores and lone pairs should contribute a bond order value of 0.

To count the total bond order of a CMO configuration is not that simple, because the nature, especially the bonding nature, of CMOs is often ambiguous; for instance, according to the sign of Mulliken's overlap population (OP),<sup>2</sup> the  $3\sigma_g$  of the  $N_2$  molecule has been variously characterized as "bonding,"<sup>1</sup> "nonbonding,"<sup>1</sup> or even "antibonding."<sup>2</sup>

In this study we show that, if a proper BO basis is chosen, one may gauge the bond order count by expressing the CMO as the linear combination of BOs (LCBO-MO). One can then easily characterize the nature of CMOs according to their BO components.

One can introduce two indices: (1) the weight of bonding orbitals, also called the Lewis bond order (LBO) and (2) the weight of lone pair orbitals (WLPO), to quantify the character of each CMO. These indices are very helpful in accounting for the photoelectron spectroscopy (PES).

The application of a LCBO-MO approximation to account for PES results has existed for some time.<sup>3</sup> However, the early applications of LCBO-MO were only limited to calculations of ionization potential. In this study, we hope to shed new light on the study of PES with the help of the LBO and WLPO indices.

## Method

In the linear combination of atomic orbital (LCAO) approximation, the CMOs are expanded in a primitive basis set,  $\{x_i\}$ :  $\psi_i = \sum c_{ij} x_j$ .

Usually, the primitive basis set  $\{x_i\}$  is chosen for convenience and thus one cannot assign any physical meaning to the expansion coefficients. In the LCBO-MO scheme we have:

$$\psi_i = \sum a_{ij} B_j \quad (1)$$

Here the basis set  $\{B_j\}$  is chosen to represent the localized core, lone pair, bonding, and antibonding orbitals in the elementary Lewis structure.

We use the notations  $k_A$  and  $n_A$  to denote the one-center (1C) BOs for the core and lone pair types centered on atom A, and  $\sigma_{AB}$  (or  $\sigma_{AB}^*$ ) and  $\pi_{AB}$  (or  $\pi_{AB}^*$ ) to denote the two-center (2C) BOs for the  $\sigma$  and  $\pi$  localized bonds (or antibonds) extending over atoms A and B.

Weinhold's natural bond orbital (NBO) method<sup>4</sup> is a powerful tool for extracting the BO basis of a Lewis structure from the density matrix of an *ab initio* wave function. Except for the minor components of the "non-Lewis" antibond and Rydberg orbital, the NBOs are very close to the corresponding naturally localized molecular orbitals (NLMO), conventionally known as localized molecular orbitals (LMO). Because the NBO basis is an orthonormal basis, the LCBO-MO expansion [eq. (1)] is very similar to the unitary transformation between CMOs and LMOs, which keeps all molecular properties invariant.

When we use Weinhold and Brunck's NBO as the BO basis to expand the CMOs,<sup>5</sup> we can define the following indices according to the weights of the BOs in this unique Lewis structure. We

define the index  $LBO^i$  of a doubly occupied CMO  $\psi_i$  as:

$$LBO^i = a_{ik}^2 \quad (2)$$

if  $B_k$  in eq. (1) is a  $\sigma_{AB}$  (or  $\pi_{AB}$ ) bonding-type, BO. We also define  $WLPO^i$  of  $\psi_i$  as:

$$WLPO_A^i = a_{il}^2 \quad (3)$$

if  $B_l$  in eq. (1) is a lone-pair-type BO on atom  $A$ .

The force constant,  $k_{AB}$ , for stretching the bond distance,  $R_{AB}$ , is related to the total LBO value:

$$LBO = \sum_i LBO^i \quad (2a)$$

For a polyatomic molecule with the force constants  $k_{AB}$ ,  $k_{BC}$  for stretching of the bond distances  $R_{AB}$ ,  $R_{BC}$ , ... one may have the total LBO values of  $LBO_{AB}$ ,  $LBO_{BC}$ , ..., or  $LBO_1$ ,  $LBO_2$ , ... if one uses the indices 1 and 2 to denote the bond  $A-B$ ,  $B-C$ , ..., etc.

In this study, the total WLPO value of concern is:

$$WLPO = \sum_i \sum_A WLPO_A^i \quad (3a)$$

## Calculations and Results

### BO CONFIGURATIONS

In this article we study the molecular systems  $N_2$ , CO, CS, NO, HCN,  $C_2H_2$ ,  $H_2O$ , and  $H_2S$ . The CMO configuration  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 \pi_u^4 3\sigma_g^2$  of  $N_2$  can be associated with a Lewis structure described by the following BO configuration:

$$k_A^2 k_B^2 n_A^2 n_B^2 \sigma^2 \pi_x^2 \pi_y^2$$

The corresponding BO configurations for the systems CO, HCN, and HCCH are:

$$\begin{aligned} k_C^2 k_O^2 n_C^2 n_O^2 \sigma^2 \pi_x^2 \pi_y^2 & \text{ for CO} \\ k_C^2 k_N^2 \sigma_{HC}^2 \sigma_{CN}^2 n_N^2 \pi_x^2 \pi_y^2 & \text{ for HCN} \\ k_A^2 k_B^2 \sigma_{HC}^2 \sigma_{CH}^2 \sigma_{CC}^2 \pi_x^2 \pi_y^2 & \text{ for HCCH} \end{aligned} \quad (4)$$

The CS molecule has a valence BO configuration similar to that of the CO molecule:

$$n_C^2 n_S^2 \sigma^2 \pi_x^2 \pi_y^2 \quad (5)$$

and, when compared with the CO molecule, the NO molecule has one more electron occupying the

$\pi_x^*$  antibonding orbital. However, the NBO analysis gives the following different orbitals for different spin (DODS)<sup>6</sup> valence BO configurations of the NO molecule:

$$n_N^2 n_O^2 \sigma^2 \pi_y^2 x_N^1 x_O^1 \bar{\pi}_x^1 \quad (6)$$

where  $x_N$  and  $n_N$  are the  $\pi$  and  $\sigma$  lone pair orbitals on atom N, and the singly occupied  $\pi$  lone pair orbitals  $x_N$  and  $x_O$  have spin  $\alpha$ , and the barred bonding orbital,  $\bar{\pi}_x^1$ , has spin  $\beta$ .

The  $H_2O$  and  $H_2S$  molecules also have a similar valence CMO configuration:

$$ka_1^2 lb_2^2 (k+1)a_1^2 lb_1^2$$

which can be transformed into the following valence BO configuration:

$$\sigma_{AH}^2 \sigma_{A'H'}^2 x_A^2 n_A^2$$

For symmetric molecules the following symmetrically adapted group orbitals (SAGO) are:

$$k^\pm = 2^{-1/2}(k_A \pm k_B) \quad (7)$$

$$n^\pm = 2^{-1/2}(n_A \pm n_B) \quad (8)$$

and:

$$\sigma^\pm = 2^{-1/2}(\sigma_{HC} \pm \sigma_{C'H'})$$

or:

$$\sigma^\pm = 2^{-1/2}(\sigma_{AH} \pm \sigma_{A'H'}) \quad (9)$$

are employed as building blocks.

We performed RHF and ROHF 6-31G calculations for molecules  $N_2$ , CO, CS, NO, HCN,  $C_2H_2$ ,  $H_2O$ , and  $H_2S$  using Gaussian-94.<sup>7</sup> Reed et al.'s NBO method<sup>4</sup> then performed the *a posteriori* analysis of the wave function to obtain the orthonormal optimal NBOs and the LCBO-MO expansions. Tables I and II show the LCBO-MO expansion of eq. (1), the  $LBO^i$  and  $WLPO^i$  values (i.e., the weights of bonding [ $\sigma$  or  $\pi$ ] and lone pair ( $n_A$  or  $n^\pm$  etc.) orbitals in the expansions according to eqs. (2) and (3).

The values of LBO and WLPO obtained using Weinhold's method do not suffer from basis-set-dependent defects like the values of OP obtained using Mulliken's method (Table I). We performed the RHF calculations for  $N_2$  and CO using the extended basis set 6-311G\*. Although the energies change from  $-108.868$  and  $-112.667$  to  $-108.969$  and  $-112.768$  a.u., respectively, for  $N_2$  and CO, their LCBO-MO expansions for the main compo-

**TABLE I.**  
**LCBO-MO Analysis of Weights of Bonding and Lone Pair Orbitals for Diatomic Molecules.<sup>a</sup>**

Molecule	LCBO-MO	WLPO <sup>i</sup>	LBO <sup>i</sup>	OP <sup>b</sup>
N <sub>2</sub>	$2\sigma_g \sim 0.94\sigma + 0.30n^+$	0.10	0.89	0.847 (0.86)
	$2\sigma_u \sim n^-$	1.0	0.00	0.148 (−0.36)
	$1\pi_x, 1\pi_y$	0.0	1.0	1.156 (0.44)
	$3\sigma_g \sim 0.31\sigma - 0.95n^+$	0.89	0.10	−0.237 (−0.08)
CO	$3\sigma \sim 0.16n_C + 0.90\sigma + 0.38n_0$	0.18	0.81	0.492 (0.74)
	$4\sigma \sim -0.30n_C - 0.32\sigma + 0.89n_0$	0.88	0.10	0.160 (−0.30)
	$1\pi_x, 1\pi_y$	0.0	1.0	0.927 (0.32)
	$5\sigma \sim 0.94n_C - 0.26\sigma + 0.22n_0$	0.93	0.07	−0.338 (−0.06)
CS	$5\sigma \sim 0.27n_C + 0.84\sigma + 0.44n_S$	0.26	0.71	
	$6\sigma \sim -0.53n_C - 0.26\sigma + 0.80n_S$	0.92	0.07	
	$2\pi_x, 2\pi_y$	0.0	1.0	
	$7\sigma \sim 0.80n_C - 0.46\sigma + 0.38n_S$	0.78	0.21	
NO	$3\sigma \sim 0.24n_N + 0.87\sigma + 0.41n_0$	0.23	0.76	
	$4\sigma \sim -0.59n_N - 0.21\sigma + 0.78n_0$	0.96	0.04	
	$5\sigma \sim 0.77n_N - 0.43\sigma + 0.47n_0$	0.81	0.18	
	$\pi_x \sim 0.51x_N + 0.86x_0$	0.0	1.0	
	$\pi_y \sim 0.57y_N + 0.82y_0$	0.0	1.0	
	$\pi_x^* \sim 0.86x_N - 0.51x_0$	0.0	−1.0	

<sup>a</sup>The internuclear distances (Å) are 1.1, 1.131, 1.534, and 1.151 for N<sub>2</sub>, CO, CS, and NO, respectively.<sup>b</sup>Data within parentheses are quoted from ref. 8; those not in parentheses are quoted from ref. 9.**TABLE II.**  
**LCBO-MO Analysis of Weights of Bonding and Lone Pair Orbitals for Polyatomic Molecules.<sup>a</sup>**

Molecule	LCBO-MO	WLPO <sup>i</sup>	LBO <sup>ic</sup>		OP <sup>id</sup>	
			LBO <sub>1</sub> <sup>i</sup>	LBO <sub>2</sub> <sup>i</sup>	O—H	H—H
H <sub>2</sub> O	$2a_1 \sim 0.85\sigma^+ + 0.52n_0$	0.27	0.36	0.36	0.34	0.0
	$1b_2 \sim \sigma^-$	0.0	0.50	0.50	0.331	−0.103
	$3a_1 \sim 0.85n_0 - 0.52\sigma^+$	0.72	0.14	0.14	0.202	0.005
	$1b_1 \sim x_0$	1.0	0.0	0.0	0.0	0.0
H <sub>2</sub> S	$4a_1 \sim 0.80\sigma^+ + 0.58n_S$	0.34	0.33	0.33		
	$2b_2 \sim \sigma^-$	0.0	0.50	0.50		
	$5a_1 \sim 0.81n_S - 0.59\sigma^+$	0.66	0.17	0.17		
	$2b_1 \sim x_S$	1.0	0.0	0.0		
HCN	$3\sigma \sim 0.16\sigma_1 + 0.94\sigma_2 + 0.25n_N$	0.06	0.03	0.88		
	$4\sigma \sim -0.97\sigma_1 + 0.11\sigma_2 + 0.21n_N$	0.04	0.94	0.01		
	$5\sigma \sim 0.18\sigma_1 - 0.28\sigma_2 + 0.94n_N$	0.88	0.03	0.08		
	$1\pi_x, 1\pi_y$	0.0	0.0	1.0 (×2)		
HCC'H' <sup>b</sup>	$2\sigma_g \sim 0.28(\sigma_1 + \sigma_3) + 0.90\sigma_2$		0.08 (×2)	0.81		
	$2\sigma_u \sim 0.70(\sigma_1 - \sigma_3) - 0.08\sigma_2^*$		0.5 (×2)	−0.00		
	$3\sigma_g \sim 0.65(\sigma_1 + \sigma_3) - 0.40\sigma_2$		0.42 (×2)	0.16		
	$1\pi_x, 1\pi_y$		0.00	1.0 (×2)		

<sup>a</sup>The internuclear distances are 0.956 Å for H<sub>2</sub>O, 1.336 Å for H<sub>2</sub>S, 1.065 Å and 1.153 Å for bonds C—H and C—N in HCN, 1.061 Å and 1.203 Å for bonds C—H and C—C in C<sub>2</sub>H<sub>2</sub>. The bond angles are 104.5° and 92.1° for H<sub>2</sub>O and H<sub>2</sub>S.<sup>b</sup>The notation (×2) denotes the values assigned to both  $1\pi_x$  and  $1\pi_y$ , or  $\sigma_1$  and  $\sigma_3$ , respectively.<sup>c</sup>The indices 1 and 2 refer to: (1) AH and AH' for HAH' molecules; (2) HC and CN for HCN; and (3) HC (C'H') and CC' for HCC'H'.<sup>d</sup>Data quoted from ref. 21.

nents change only slightly; for example:

		6-31G	6-311G*
N <sub>2</sub>	2σ <sub>g</sub>	0.9421σ + 0.3032n <sup>+</sup>	0.9404σ + 0.3083n <sup>+</sup>
	3σ <sub>g</sub>	0.3121σ - 0.9475n <sup>+</sup>	0.3169σ - 0.9463n <sup>+</sup>
CO	3σ	0.1617n <sub>C</sub> + 0.9022σ + 0.3754n <sub>O</sub>	0.1468n <sub>C</sub> + 0.8973σ + 0.3923n <sub>O</sub>
	4σ	-0.2967n <sub>C</sub> - 0.3203σ + 0.8938n <sub>O</sub>	-0.2720n <sub>C</sub> - 0.3469σ + 0.8921n <sub>O</sub>

This is in strong contrast to the OP results of Table I. The OP results obtained by using the minimum basis set (data within brackets)<sup>8</sup> differ significantly from those using the extended basis set (data without brackets)<sup>9</sup>.

LBO VALUES

The diatomic molecule has only one stretching vibration mode with the force constant *k* reflecting the bonding strength, which can be related to the total bond order of the Lewis structure. The removal of an electron from CMO ψ<sub>*i*</sub> with LBO<sup>*i*</sup> > 0 will decrease the total LBO and *k* values. When the change of force constant is significant, the ionic state, ψ<sub>*i*</sub><sup>-1</sup>, should have a stretching frequency less than that of the neutral molecule, ν(*I*) < ν(*M*) (*I* and *M* denote the positive ion and neutral molecule, respectively).

There are two vibration modes discernible in the vibrational structures of HCN and C<sub>2</sub>H<sub>2</sub> (or C<sub>2</sub>D<sub>2</sub>). For the HCN molecule the vibration modes, ν<sub>1</sub> and ν<sub>2</sub>,<sup>1</sup> for C—H and C—N stretchings, have the force constants of *k*<sub>1</sub> and *k*<sub>2</sub>, reflecting the bond strengths in bond regions 1 and 2 (C—H and C—N regions) in HCN.

For the H—C—C'—H' molecule the symmetric stretching mode, ν<sub>1</sub>, has the same force constant, *k*<sub>1</sub>, for both regions 1 and 3 (H—C and C'—H' regions), whereas ν<sub>2</sub> has the force constant *k*<sub>2</sub> for C—C' stretching.

The frequency changes Δν<sub>1</sub> and Δν<sub>2</sub> in the PES of HCN and C<sub>2</sub>H<sub>2</sub> can also be accounted for by the LBO value changes within bond regions 1 and 2. Here we use the indices 1 and 2 to denote the bond regions in HCN and C<sub>2</sub>H<sub>2</sub>. One may find that the value of Δν<sub>*j*</sub> < 0 in Table V correlates very well with the value of LBO<sup>*j*</sup> in Table II.

The bent HAH' molecule has three normal vibrational modes. Both symmetric and antisymmet-

ric stretching modes, ν<sub>1</sub> and ν<sub>3</sub>, are related to the stretching force constants *k*<sub>AH</sub> = *k*<sub>AH'</sub>, whereas the bending mode is related to the force constant *k*<sub>θ</sub>. One may use the LBO values of the BOs σ<sub>AH</sub> and σ<sub>AH'</sub> to account for the force constants *k*<sub>AH</sub> = *k*<sub>AH'</sub> for both symmetric and antisymmetric stretching modes ν<sub>1</sub> and ν<sub>3</sub>.

Because of orbital interaction a σ-type CMO, ψ<sub>*i*</sub>, may consist of several lone pair and bonding type BOs, *n*<sub>A</sub> and σ<sub>AB</sub>, etc. For instance, 3σ<sub>g</sub> of C<sub>2</sub>H<sub>2</sub> has the following LCBO expansion: 3σ<sub>g</sub> ~ 0.65 · (σ<sub>1</sub> + σ<sub>3</sub>) - 0.40σ<sub>2</sub>, with the values LBO<sub>1</sub> = 2 × (0.65)<sup>2</sup> and LBO<sub>2</sub> = (0.40)<sup>2</sup> relating to the values of *k*<sub>1</sub> and *k*<sub>2</sub> for the stretching modes ν<sub>1</sub> and ν<sub>2</sub>. The removal of an electron from 3σ<sub>g</sub> decreases both force constant values of *k*<sub>1</sub> and *k*<sub>2</sub> significantly and thus the ionic state 3σ<sub>g</sub><sup>-1</sup> of C<sub>2</sub>D<sub>2</sub> has ν<sub>1</sub>(*I*) = 2500 cm<sup>-1</sup> and ν<sub>2</sub>(*I*) = 1370 cm<sup>-1</sup>.<sup>11</sup> These are less than the respective values of ν<sub>1</sub>(*M*) = 2683 and ν<sub>2</sub>(*M*) = 1761 cm<sup>-1</sup> for the neutral molecule.<sup>11</sup>

WLPO VALUES

Because the vibrational structures of many PES bands are unresolvable, we can only compare the weight of bonding orbitals with a few PES results. It is noteworthy that the present method can also correctly relate the weight of lone pair orbitals in CMO to the relative intensities in Penning ionization electron spectroscopy (PIES).<sup>12</sup> It has been noted that the relative intensities in PIES bands are in proportion to the charge spreading outside the molecular surface by their CMOs.<sup>12</sup>

The charge spreading outside the molecular surface by the BOs should follow the order: *n* > π > σ, which is precisely the opposite order of the exchange charge accumulated in the bonding region. Therefore, one may use the weight of lone pair orbitals, the index WLPO<sup>*i*</sup>, to measure the charge spreading outside by the given CMO.

We tabulate the values of WLPOs and the PIES band intensity ratios in Table III.

<sup>1</sup>One usually uses ν<sub>3</sub>, instead of ν<sub>2</sub> to denote the C—N stretching mode of the HCN molecule.<sup>10</sup>

**TABLE III.**  
**PIES Intensity Enhancement Analysis.**

Molecule	WLPO <sup>i</sup> <sup>a</sup>	PIES band intensity ratio <sup>b</sup>	EED ratio <sup>b</sup>
N <sub>2</sub>	0.10 (2σ <sub>g</sub> )		
	1.00 (2σ <sub>u</sub> )	1.00	1.00
	0.00 (1π <sub>x</sub> , 1π <sub>y</sub> )	0.36	1.06
	0.89 (3σ <sub>g</sub> )	0.90	1.23
CO	0.18 (3σ)		
	0.88 (4σ)	0.43	0.50
	0.00 (1π <sub>x</sub> , 1π <sub>y</sub> )	0.20	0.53
	0.93 (5σ)	1.00	1.00
HCN	0.06 (3σ)		
	0.04 (4σ)		
	0.88 (5σ)		
	0.00 (1π <sub>x</sub> , 1π <sub>y</sub> )		
	<i>t</i> <i>c</i>		
HCC'H'	0.5 (×2)      0.0 (2σ <sub>u</sub> )	0.68	0.52
	0.42 (×2)      0.16 (3σ <sub>g</sub> )	0.51	0.52
	0.00      1.0 (1π <sub>x</sub> , 1π <sub>y</sub> )	1.00	1.00
H <sub>2</sub> O	0.0 (1b <sub>2</sub> )	0.48	0.72
	0.72 (3a <sub>1</sub> )	1.00	1.00
	1.0 (1b <sub>1</sub> )	0.61	1.23
H <sub>2</sub> S	0.0 (2b <sub>2</sub> )	0.44	0.83
	0.66 (5a <sub>1</sub> )	0.70	0.84
	1.0 (2b <sub>1</sub> )	1.00	1.00

<sup>a</sup>The WLPO<sup>i</sup> values are tabulated in the same order as the third columns of Tables I and II. The data for C<sub>2</sub>H<sub>2</sub> are the LBO<sup>i</sup> values for the terminal (*t*) and central (*c*) bonds in Table II.

<sup>b</sup>Quoted from ref. 12.

## Discussion

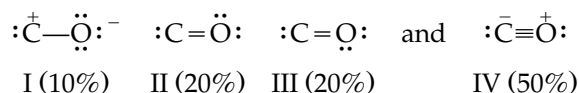
### FLEXIBILITY OF BO BASIS

For a diatomic molecule, AB, the NBO method is always able to produce a unique Lewis structure, because the AB molecule may have only the following simple 2C bonding orbitals:

$$\sigma = C_A h_A + C_B h_B \text{ and } \pi = D_A x_A + D_B x_B \quad (10)$$

where  $h_A$  and  $h_B$  are the  $\sigma$ -type bonding pair hybrid orbitals;  $x_A$  and  $x_B$  are the  $\pi$ -type bonding pair orbitals; and  $C_A$  and  $D_A$  (or  $C_B$  and  $D_B$ ) are the polarization coefficients, whose squares give the charge densities associated with atom A (or B). Therefore, the partial ionic character of the polar bonds can be described by the polarization coefficients in the LCBO-MO method, whereas it has to be described by several resonating Lewis structures in the VB theory.

For the CO molecule, the VB theory uses the following four resonating Lewis structures<sup>13</sup>:



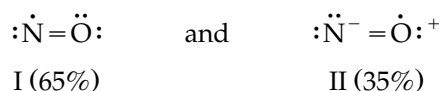
to describe the bond order and the partial ionic character of the bonds. The CMO configuration of the RHF wave function for CO can be very well (99.9%) transformed into a BO configuration (4) of the most important Lewis structure (IV) by Weinhold's method. Therefore, we use the BO basis of the Lewis structure (IV) to expand the CMOs of CO.

The BO configuration (4) has a total LBO value of 3, and the following polarization coefficients for the C and O atoms:

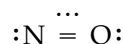
$$\begin{array}{cc} 0.5326 \text{ and } 0.8463 (\sigma \text{ type}) \text{ and} \\ 0.4569 \text{ and } 0.8895 (\pi \text{ type}) \end{array}$$

which are used to describe the partial ionic character of the BOs  $\sigma$  and  $\pi$ .

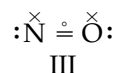
NO is a stable radical with a delocalized, unpaired electron described by the following resonating Lewis structures<sup>14</sup>:



The CMO configuration of the ROHF wave function for NO can also be very well (99.9%) transformed into a DODS-type BO configuration (6).<sup>6</sup> The strong resonance between structures I and II can be well described by a single structure with a three-electron (3e) bond unit,  $\pi_x^2 \pi_x^{*1}$ , or its BO equivalent,  $x_N^1 x_O^1 \bar{\pi}_x^1$  (see ref. 13):



Interestingly, the BO configuration (6) is in accord with the Linnett structure:



where the two  $\times$  characters denote the two  $\pi$ -type lone pair orbitals  $x_N$  and  $x_O$  of the  $\alpha$  spin, whereas  $o$  denotes the bonding orbital  $\bar{\pi}_x$  of the  $\beta$  spin.<sup>15</sup> The BO configuration (6) and the Linnett structure (III) reveal that NO has a total LBO value of 2.5 due to  $\sigma^2 \pi_y^2 \bar{\pi}_x^1$ . After proper spin coupling of the 3e bond unit, there should be only one spin-un-

paired lone pair orbital for the doublet state  $^2\Pi$  of the NO molecule. Substituting  $\bar{\pi}_x = c_I \bar{x}_N + c_{II} \bar{x}_O$  into the 3e bond unit, the resonance between structures I and II results from:

$$x_N^1 x_O^1 \bar{\pi}_x^1 = c_I x_N^2 x_O + c_{II} x_N x_O^2$$

By using Weinhold's LCBO-MO expansion coefficients  $c_I = 0.51$  and  $c_{II} = 0.86$  from Table I, the weights  $c_I^2 = 26\%$  and  $c_{II}^2 = 73\%$  are in reasonable agreement with the results of 35% and 65% obtained from the electron spin resonance spectrum.<sup>14</sup>

### ANALOGOUS PAIRS ( $N_2$ , $C_2H_2$ ) AND (CO, HCN)

The symmetric molecules  $N_2$  and  $C_2H_2$  have the same CMO configuration. When one compares the valence CMOs of  $N_2$  and  $C_2H_2$ , one may find the following correlation between the BOs:

$N_2$	$C_2H_2$
$2\sigma_g \sim \sigma_{NN}$	$2\sigma_g \sim \sigma_{CC}$
$2\sigma_u \sim n^-$	$2\sigma_u \sim \sigma^-$
$\pi = \pi_{NN}$	$\pi = \pi_{CC}$
$3\sigma_g \sim n^+$	$3\sigma_g \sim \sigma^+$

When one compares the CMOs of CO and HCN, one may also find the following correlation between BOs:

CO	HCN
$3\sigma \sim \sigma$	$3\sigma \sim \sigma_2 \equiv \sigma_{CN}$
$4\sigma \sim n_O$	$5\sigma \sim n_O$
$5\sigma \sim n_C$	$4\sigma \sim \sigma_1 \equiv \sigma_{HC}$
$\pi = \pi_{CO}$	$\pi = \pi_{CN}$

Here we use the notations  $2\sigma_g \sim \sigma_{NN}$ , etc., to identify the main component  $\sigma_{NN}$  as the character of  $2\sigma_g$ , whereas the notations  $\sigma^\pm$  and  $n^\pm$  are those given in eqs. (8) and (9). The fact that both the reverse orbital energy orders  $2\sigma_u \sim n^- < 3\sigma_g \sim n^+$  and  $2\sigma_u \sim \sigma^- < 3\sigma_g \sim \sigma^+$  can be accounted for by the through bond interaction (TBI)<sup>16</sup> manifests the importance of TBI in both diatomic<sup>17</sup> and polyatomic molecules.<sup>16</sup>

### SPREADING CHARGES AND BAND INTENSITIES OF PIES

Because the exchange charge accumulated in the bonding regions is in proportion to the bond strength, the relative intensity orders of  $\pi > \sigma$  are found in most molecules that have the opposite

bond strength order of  $\sigma > \pi$ . The reverse intensity order  $1.0 > 0.90 > 0.36$  for the  $2\sigma_u$ ,  $3\sigma_g$ , and  $\pi_u$  bands of the  $N_2$  molecule appears quite unexpectedly.<sup>12</sup> It had been speculated that  $\sigma$  and  $\pi$  symmetry is not decisive in PIES.<sup>12</sup>

According to the LCBO-MO method, the  $\sigma$ -type CMO may also consist of lone pair components with the charge spreading outside the molecular surface even more than that of  $\pi$ -MO. The band intensity ratio of  $1.0 > 0.90 > 0.36$  can be accounted for by the WLPO<sup>i</sup> values 1.00, 0.89, and 0.00 for the CMOs  $2\sigma_u$ ,  $3\sigma_g$ , and  $\pi_u$  for the  $N_2$  molecule (Table III).

The observed relative intensity order  $5\sigma > 4\sigma$  in CO can also be accounted for by their WLPO<sup>i</sup> values of  $0.93(5\sigma) > 0.88(4\sigma)$  (Table III).

The charge spreading outside the molecular surface has also been directly calculated, and is referred to as the exterior electron distribution (EED).<sup>12</sup> The results in Table III show that the WLPO<sup>i</sup> values account for the intensity ratio better than those with EED.

Analysis of the PIES and PES bands of HCN was complicated by the superposition of  $1\pi^{-1}$  and  $5\sigma^{-1}$  bands.<sup>18</sup> Because  $5\sigma$  is mainly a lone pair orbital with the WLPO<sup>i</sup> value of 0.88, one would expect that the PIES results display different band intensities due to  $\pi$  and lone pair orbitals if the two bands are not overlapping. Indeed, the PIES results confirm that the lone pair band has more intensity than that of the  $\pi$  band<sup>18</sup> for  $CH_3CN$ , whose two bands do not overlap. There is no lone pair in  $C_2H_2$ . Therefore, the  $\pi$  band has more intensity than the  $\sigma$  bands. There are three  $\sigma$  bonds in  $C_2H_2$ : among them,  $\sigma_1 = \sigma_{HC}$  and  $\sigma_3 = \sigma_{C'H'}$  are the two terminal bonds (denoted by  $\sigma^t$ ), and both  $\sigma_2 = \sigma_{CC}$  (denoted by  $\sigma^c$ ) and  $\pi_{CC}$  are the central bonds. Because  $C_2H_2$  has no lone pair orbital we may use the weights of BOs for terminal bonds (*t*) LBO<sub>1</sub><sup>i</sup> and central bond (*c*) LBO<sub>2</sub><sup>i</sup> in Table I to compare the spreading charges of  $\sigma$ -type CMOs. Apparently, the charges in  $\sigma^t$  should have a greater chance than  $\sigma^c$  to spread outside the molecular surface. Therefore, it is plausible to compare the spreading charge according to the weight of  $\sigma^t$  for  $C_2H_2$ . Table III gives the values 0.5 and 0.42 for the weights of  $\sigma^t$  in  $2\sigma_u$  and  $3\sigma_g$ , which correlate very well with the intensities 0.68 and 0.51 for these two bands.<sup>12</sup>

The  $H_2O$  (or  $H_2S$ ) molecule has two lone pair orbitals,  $n_O$  and  $x_O$  (or  $n_S$  and  $x_S$ ). Even though the  $3a_1$  orbital has a lower WLPO<sup>i</sup> value than  $1b_1$  (0.72 vs. 1.0), the charge spread outside the molecular surface by the *s*-rich  $n_O$  is more than that of

the pure  $2p_x$  orbital  $x_O$ . Thus, one has the intensity ratio of 1.0 vs. 0.61 for the  $3a_1^{-1}$  and  $1b_1^{-1}$  bands of  $H_2O$ . The reverse intensity ratio (0.7 vs. 1.0) for the  $5a_1^{-1}$  and  $2b_1^{-1}$  bands of  $H_2S$  can be accounted for by the fact that  $3p_x$  in  $H_2S$  spreads more charge than  $2p_x$  in  $H_2O$ . It has been pointed out that  $2p_x$  in  $H_2O$  is more compact because it can penetrate into the core containing no  $p_x$ -type AO, whereas  $3p_x$  in  $H_2S$  is more extended because it is repelled by the core containing  $2p_x$  AO.<sup>20</sup>

## LBO VALUES AND VIBRATIONAL STRUCTURES OF PES

The diatomic molecule has a stretching vibrational frequency,  $\nu(M)$ . The removal of an electron from CMO  $\psi_i$  gives rise to an ionic state,  $\psi_i^{-1}$ , with the vibrational frequency,  $\nu(I)$ .

For the  $N_2$  molecule, one obtains a vibrational frequency of  $\nu(M) = 2331\text{ cm}^{-1}$  for the neutral molecule,  $\nu(I) = 2175\text{ cm}^{-1}$  and  $\Delta\nu = 2175 - 2331 = -156\text{ cm}^{-1}$  for the ionic state  $3\sigma_g^{-1}$ ,  $\nu(I) = 1850\text{ cm}^{-1}$  and  $\Delta\nu = 1850 - 2331 = -481\text{ cm}^{-1}$  for the ionic state  $1\pi_u^{-1}$ ,  $\nu(I) = 2373\text{ cm}^{-1}$  and  $\Delta\nu = 2373 - 2331 = +42\text{ cm}^{-1}$  for the ionic state  $2\sigma_u^{-1}$ .<sup>19</sup> These results can be accounted for by the LBO<sup>*i*</sup> values 0.1, 1.0, and 0.0 for  $3\sigma_g$ ,  $\pi_u$ , and  $2\sigma_u$ , respectively (Table I).

The bonding nature of the CMO had also been analyzed according to the overlap population (OP).<sup>9</sup> OP has also been used to account for the vibrational structures of PES.<sup>21</sup> However, OP as well as Mulliken population analysis fail to give a useful and reliable description of charge distribution in many cases.<sup>9</sup> For instance, the CMO  $2\sigma_u$  of  $N_2$  has been characterized according to its OP value as "bonding" with the OP value of 0.148,<sup>9</sup> as well as "antibonding" with the OP value of  $-0.36$ <sup>8</sup> where different OP values have been obtained by calculations using different basis sets.

The PES result of negligible value of  $\Delta\nu$  for ionizing a  $2\sigma_u$  electron is better accounted for by the nonbonding character of  $2\sigma_u$  assigned according to the LBO<sup>*i*</sup> value of 0 for  $2\sigma_u$ .

The CMOs  $2\sigma_g$ ,  $2\sigma_u$ , and  $3\sigma_g$  of  $N_2$  have usually been denoted as  $\sigma_g(s)$ ,  $\sigma_u(s)$ , and  $\sigma_g(z)$ , implying that the last one has stronger bonding character. However, the small values of  $\Delta\nu$  and short progressions indicate that  $2\sigma_u$  and  $3\sigma_g$  are essentially nonbonding, whereas the evidence in x-ray photoelectron spectroscopy indicates that  $2\sigma_g$  is strongly bonding.<sup>22</sup>

The essential nonbonding character of  $2\sigma_u$  and  $3\sigma_g$  can also be accounted for by the  $s$ - $p$  mixing

(or hybridization) concept.<sup>23</sup> However, the useful LBO<sup>*i*</sup> and WLPO<sup>*i*</sup> indices can only be obtained by the LCBO-MO method employing Weinhold's NBO orbital set.

Because the  $N_2$  and CO molecules are very similar, the valence configuration  $2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$  for  $N_2$  is also very similar to that of  $3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$  for CO. However, the correspondence between  $2\sigma_u$  and  $4\sigma$  is not quite exact, because  $4\sigma$  has an LBO value of  $0.1 = (0.32)^2$ , implying that  $4\sigma$  is a weak bonding orbital, instead of being "nonbonding," like  $2\sigma_u$  of  $N_2$ . The  $\Delta\nu$  value of  $1678 - 2143 = -465\text{ cm}^{-1}$ <sup>19</sup> for the ionic state  $4\sigma^{-1}$  is in accord with the weak bonding nature of  $4\sigma$ .

The second ( $1\pi^{-1}$ ) bands of the PES of  $N_2$  and CO have the largest magnitude of  $\Delta\nu$ , in accord with the largest LBO<sup>*i*</sup> value of 1 for the  $1\pi$  CMO. However, the third ( $6\sigma^{-1}$ ) band of the PES of CS has the largest magnitude of  $\Delta\nu$ , not in accord with the small LBO<sup>*i*</sup> value of  $6\sigma$ .

The abnormal character of the third and fourth bands for the PES of CS has been attributed to the strong configuration interaction effect in the  $^2\Sigma$  ionic state of  $CS^+$ .<sup>24</sup>

For the HCN molecule,  $4\sigma$  is mainly  $\sigma_{HC}$  with LBO<sup>*i*</sup><sub>1</sub> = 0.94, and the ionic state  $4\sigma^{-1}$  has  $\Delta\nu_1 = 1690 - 3311 = -1621\text{ cm}^{-1}$  for the C—H stretching mode.<sup>11</sup>  $1\pi$  is  $\pi_{CN}$  with LBO<sup>*i*</sup><sub>2</sub> = 1.0 and the ionic state  $1\pi^{-1}$  has  $\Delta\nu_2 = 1800 - 2097 = -297\text{ cm}^{-1}$  for the C—N stretching mode.<sup>11</sup> For the HCC'H' molecule,  $1\pi$  is  $\pi_{CC'}$  with LBO<sup>*i*</sup><sub>2</sub> = 1.0, the ionic state  $1\pi^{-1}$  has  $\Delta\nu_2 = 1830 - 1983 = -153\text{ cm}^{-1}$ ,<sup>11</sup> whereas the ionic state  $1\pi^{-1}$  of DCC'D' has  $\Delta\nu_2 = 1610 - 1761 = -151\text{ cm}^{-1}$  for the C—C' stretching mode.<sup>11</sup>  $3\sigma_g$  consists of two  $g$ -type orbitals,  $\sigma^+ = 2^{-1/2}(\sigma_1 + \sigma_3)$  and  $\sigma_{CC'} = \sigma_2$ , with LBO<sup>*i*</sup><sub>1</sub> = 0.83 for  $\sigma^+$  and LBO<sup>*i*</sup><sub>2</sub> = 0.16 for  $\sigma_{CC'}$ . The ionic state  $3\sigma_g^{-1}$  of DCC'D' has  $\Delta\nu_1 = 2500 - 2683 = -183\text{ cm}^{-1}$  and  $\Delta\nu_2 = 1370 - 1761 = -391\text{ cm}^{-1}$  for both the C—D and C—C' stretching mode.<sup>11</sup>  $2\sigma_u$  consists mainly of one  $u$ -type orbital  $\sigma^- = 2^{-1/2}(\sigma_1 - \sigma_3)$  with LBO<sup>*i*</sup><sub>1</sub> = 1.0. The ionic state  $2\sigma_u^{-1}$  of HCC'H' has  $\Delta\nu_1 = 1900 - 3369 = -1469\text{ cm}^{-1}$  and  $\Delta\nu_2 = 2510 - 1983 = +527\text{ cm}^{-1}$ , whereas DCC'D' has  $\Delta\nu_1 = 1420 - 2683 = -1263\text{ cm}^{-1}$  and  $\Delta\nu_2 = 2290 - 1761 = +529\text{ cm}^{-1}$ .<sup>8</sup> Within the LCAO-MO scheme one may account for the antibonding character of the C—C' bond ( $\Delta\nu_2 > 0$ ) in terms of an out-of-phase combination of two AOs for carbon atoms in  $2\sigma_u$ . Within the LCBO-MO scheme one has to account for it in terms of the weight of antibonding BO



$\sigma_{CC}^*$ . Even though there is a small component of  $\sigma_{CC}^*$  in  $2\sigma_u$ , the negligible weight of  $\sigma_{CC}^*$  seems incapable of accounting for the large  $\Delta\nu_2 > 0$ . It seems more plausible to account for  $\Delta\nu_2 > 0$  by TBI.<sup>16</sup> Because  $\sigma^-$  and  $\sigma_{CC}^*$  have energies of  $-0.8066$  a.u. and  $+1.3737$  a.u., the consequence of TBI is that the upper-lying  $\sigma_{CC}^*$  is pushed further up, whereas the underlying  $\sigma^-$  values are pressed further down. One may conjecture that the repelling of the two energy levels is accompanied by charge redistribution. After TBI, the charge in the C—C' region is shifted to the regions H—C and C'—H', such that the H—C and C'—H' bonds become more stable with the  $LBO_{HC}^i = LBO_1^i > 0$  value, and the C—C' bond becomes less stable with the  $LBO_{CC'}^i = LBO_2^i < 0$  value.

The charge redistribution caused by TBI can also account for the  $\Delta\nu_1 = -1263\text{ cm}^{-1}$  of the  $2\sigma_u^{-1}$  ionic state<sup>11</sup> ( $LBO_1^i = 1.0$ ) being much larger than that of  $\Delta\nu_1 = -183\text{ cm}^{-1}$  of the  $3\sigma_g^{-1}$  ionic state<sup>11</sup> ( $LBO_1^i = 0.83$ ) in DCC'D'. The consequence of TBI in  $3\sigma_g$  is that the underlying  $\sigma_{CC'}$  is repelled further down by the upper-lying  $\sigma^+$ . Because  $\sigma_{CC'}$  now lies below  $\sigma^+$ , the charge redistribution accompanying the repelling levels is now in just the opposite direction. After TBI and charge redistribution, the perturbed BOs  $\sigma'_{HC}$  and  $\sigma'_{C'H'}$  in  $2\sigma_u$  differ from those of perturbed BOs  $\sigma''_{HC}$  and  $\sigma''_{C'H'}$  in  $3\sigma_g$ , because the former ones have charge shifting from the C—C' region into the H—C and C'—H' regions, whereas the latter ones have charge shifting in the opposite direction. Therefore,  $2\sigma_u$  has more stable perturbed  $\sigma'_{HC}$  and  $\sigma'_{C'H'}$  bonds than those of  $3\sigma_g$ .

For bent HAH' molecules, the values of  $OP_{AH}$  and  $OP_{HH'}$  have been used to measure the bonding strength of stretching the distances  $R_{AH}$  and  $R_{HH'}$ .<sup>21</sup> Because the change in distance  $R_{HH'}$  relates directly to the change in the bond angle,  $\theta$ , one may account for the change  $\Delta\nu_2 < 0$  for the bending mode in terms of the removal of an electron from the orbital with  $OP_{HH'} > 0$ .

The results  $\Delta\nu_1 < 0$  for the  $2b_2$  and  $5a_1$  bands in the PES of  $H_2S$  can be accounted for by the fact that both  $2b_2$  and  $5a_1$  CMOs have the values  $OP_{AH} > 0$ . The results of  $\Delta\nu_2 < 0$  for the  $3a_1^{-1}$  (or  $5a_1^{-1}$ ) band can also be accounted for by the fact that the  $3a_1$  (or  $5a_1$ ) CMO has the value of  $OP_{HH'} > 0$ , whereas  $\Delta\nu_2 > 0$  for the  $1b_2^{-1}$  (or  $2b_2^{-1}$ ) band can be accounted for by the value  $OP_{HH'} < 0$ .

The results in Tables I and II show that  $\Delta\nu < 0$  for  $R_{AB}$  stretching vibration can be better accounted for by the  $LBO_{AB}^i$  value than by the  $OP_{AB}$  value.

There is no LBO value to account for  $\Delta\nu < 0$  for the bending mode. Because the Lewis structure reveals only the major feature of the bonding character, it usually discards the minor, nonbonded interaction between atoms H and H'. However, one may use either the value of  $WLPO^i$  for the  $\sigma$ -type lone pair orbital  $n_A$ , or the weight of  $\sigma^+$  (or  $\sigma^-$ ) from eq. (9) to account for the change ( $\Delta\nu$ ) in the bending mode. The first option may be chosen because the removal of an  $n_A$  electron results in the increase of the bond angle,  $\theta$ , and thus  $n_A$  has also been termed the angle-determining orbital.<sup>17</sup> The second option may be chosen because  $\sigma^+$  and  $\sigma^-$  have different nonbonded interactions revealed by their Fock matrix elements. Instead of the  $OP_{HH'}$  value, one may use  $F_{HH'}$  (the Fock matrix element in Weinhold's or-

TABLE IV. Vibrational Fine Structure Analysis for PES of Diatomic Molecules.

Molecule	$LBO^i$ <sup>a</sup>	Vibrational frequency ( $\text{cm}^{-1}$ ) $\nu$	Vibrational frequency change ( $\text{cm}^{-1}$ ) $\Delta\nu$
$N_2$	0.89 ( $2\sigma_g$ )		
	0.00 ( $2\sigma_u$ )	2373 <sup>b</sup>	+42
	1.00 ( $1\pi_x, 1\pi_y$ )	1850	-481
	0.10 ( $3\sigma_g$ )	2175	-156
		2331 ( <i>M</i> )	
$CO$	0.81 ( $3\sigma$ )		
	0.10 ( $4\sigma$ )	1678 <sup>b</sup>	-465
	1.00 ( $1\pi_x, 1\pi_y$ )	1535	-608
	0.07 ( $5\sigma$ )	2184	+41
$CS$		2143 ( <i>M</i> )	
	0.71 ( $5\sigma$ )	1050 <sup>c</sup>	-222
	0.07 ( $6\sigma$ )	840	-432
	1.0 ( $2\pi$ )	984	-288
	0.21 ( $7\sigma$ )	1330	+58
$NO$		1272 ( <i>M</i> )	
	0.76 ( $3\sigma$ )		
	0.04 ( $4\sigma$ )		
	0.18 ( $5\sigma$ )	1602 <sup>d</sup>	-302
	1.0 ( $1\pi$ )	1278	-626
	-1.0 ( $1\pi^*$ )	2376	+472
		1904 ( <i>M</i> )	

<sup>a</sup>The  $LBO^i$  values are tabulated in the same order as in the fourth column of Table I.

<sup>b</sup>Data quoted from ref. 19.

<sup>c</sup>Data quoted from ref. 24.

<sup>d</sup>There are several nearly degenerate ionic states of various multiplets resulting from removal of an electron from  $1\pi$  (or  $5\sigma$ ) CMO of the  $^2\Pi$  ground state of NO. The  $\nu(I)$  values given are the lowest of the multiplets quoted from ref. 10.

**TABLE V.** Normal Vibrational Frequencies  $\nu_i(I)$  and  $\nu_i(M)$  Observed in PES for Polyatomic Molecules.<sup>a</sup>

	$\nu_1$	$\nu_2$	$\nu_3$	$\Delta \nu_1$	$\Delta \nu_2$
$\text{H}_2\text{O}^b$					
$1A$	3652	1595	3756		
$1b_1^{-1}$	$3200 \pm 50$	$1380 \pm 50$		-452	-215
$3a_1^{-1}$		$975 \pm 50$			-620
$1b_2^{-1}$	$2990 \pm 100$	$1610 \pm 100$		-662	+15
$\text{H}_2\text{S}^b$					
$1A$	2615	1183	2684		
$2b_1^{-1}$	$2380 \pm 50$			-235	
$5a_1^{-1}$	$2040 \pm 50$	$940 \pm 50$		-575	-243
$2b_2^{-1}$	$1900 \pm 100$	$1470 \pm 100$		-715	+287
$\text{HCN}^c$					
$1\Sigma$	3311	2097			
$1\pi^{-1}$		1800			-297
$5\sigma^{-1}$					
$4\sigma^{-1}$	1690			-1621	
$\text{HCC'H}^d$ (DCC'D')					
$1\Sigma_g$	3369 (2683)	1983 (1761)			
$1\pi_u^{-1}$		1830 (1610)			-153 (-151)
$3g_g^{-1}$	(2500)	(1370)		(-183)	(-391)
$2\sigma_u^{-1}$	1900 (1420)	2510 (2290)		-1469 (-1263)	+527 (+529)

<sup>a</sup> $\Delta \nu_i = \nu_i(I) - \nu_i(M)$ , where  $\nu_i(I)$  and  $\nu_i(M)$  refer to the frequencies of the  $i$ th mode for the ion and neutral molecule. All values are given in units of  $\text{cm}^{-1}$ .

<sup>b</sup>Data quoted from ref. 25.

<sup>c</sup>Data quoted from ref. 11.

<sup>d</sup>Data quoted from ref. 11. Values given in parentheses refer to the DCC'D' molecule.

thogonal basis sets) to better account for the bond angle change  $\Delta\theta$ . Because the BO  $\sigma_{\text{AH}}$  (or  $\sigma_{\text{A'H'}}$ ) consists of the hybrid orbital  $h_{\text{A}}$  on atom A and  $1s$  AO on atom H (or H'):

$$\begin{aligned}\sigma_{\text{AH}} &= c_{\text{A}}(h_{\text{A}}) + c_{\text{H}}(1s_{\text{H}}) \text{ or} \\ \sigma_{\text{A'H'}} &= c_{\text{A}}(h_{\text{A'}}) + c_{\text{H}}(1s_{\text{H'}})\end{aligned}$$

where the hybrid orbitals,  $h_{\text{A}}$  and  $h_{\text{A'}}$ , are directed toward two AOs,  $1s_{\text{H}}$  and  $1s_{\text{H'}}$ , of different atoms H and H'.

The SAGO  $\sigma^+$  (or  $\sigma^-$ ) of eq. (9) has the following Fock matrix elements:  $F_{\text{AH}}$ ,  $F_{\text{A'H'}}$ , and  $F_{\text{HH'}}$  with the magnitudes  $|F_{\text{AH}}| = |F_{\text{A'H'}}| \gg |F_{\text{HH'}}|$ , manifesting the bonded A—H and A'—H' interactions much stronger than that of the nonbonded H—H' one. Furthermore,  $\sigma^+$  and  $\sigma^-$  have different nonbonded interactions manifested in different Fock matrix elements,  $F_{\text{HH'}}$ , due to the in-phase and out-of-phase combinations of  $1s$  AO of atoms H and H', respectively. The preliminary results show

that one may predict the effect of removing an electron from a CMO using the criteria of its  $F_{\text{HH'}}$  value in the same manner as that of  $\text{OP}_{\text{HH'}}$ .

## Concluding Remarks

The NBO method can very well (over 99%) transform a CMO set into a BO set of a unique Lewis structure. The character of the polar bond has to be described by several resonating Lewis structures in VB theory; while the polarization coefficients in eq. 10 enable the BO set of the present method to describe the various ionic character of the polar bond with ease.

Although the CMO calculation neglects important electron correlation, relaxation, and relativistic effects, the LBO and WLPO indices, quantifying the characters of  $n_{\text{A}}$ ,  $\sigma_{\text{AB'}}$ , and  $\pi_{\text{AB}}$  for each CMO, can comprehensively account for both the vibrational structure of PES and the intensity ratio of

PIES. However, the precise estimates of force constants and bond energies are beyond the capability of the present method. At present, our method works adequately for simple molecules described well by a unique Lewis structure. However, we have difficulty with polyatomic molecules having multicentered bonds for which Weinhold's NBO method fails to produce a unique Lewis structure.

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